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Composite Bearing and Seal Materials for Advanced Heat Engine Applications to 900 °C

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APPLICATIONS TO 900 °C

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ABSTRACT

Plasma sprayed composite coatings of metal-bonded chromium carbide with additions of silver and thermochemically stable fluorides were previously reported to be lubricative in pin on disk bench tests from room temperature to 900 °C. An early coating formulation of this type, designated as PS200, was successfully tested as a cylinder coating in a Stirling engine at a TRRT of 760 °C (1450 °F) in a hydrogen atmosphere, and as a backup lubricant for gas bearings to 650 °C (1250 °F). A subsequent optimization program has shown that tribological properties are further improved by increasing the solid lubricant content. The improved coating is designated as PS212. The same powder formulation has been used to make free-standing powder metallurgy (PM212) parts by sintering or hot isostatic pressing. The process is very attractive for making parts that cannot be readily plasma sprayed such as bushings and cylinders that have small bore diameters and/or high length to diameter ratios. The properties of coatings and free-standing parts fabricated from these powders are reviewed.

INTRODUCTION

This paper updates development and application test results with PS200 and PS212 plasma-sprayed composite coatings that have demonstrated self-lubricating capability from low temperature to 900 °C. The formulation and the basic friction and wear properties of PS200 were described at the last DOE workshop on coatings for advanced heat engines (Ref. 1). The two compositions differ only in the amount of solid lubricant they contain within a metal-bonded chromium carbide matrix. PS200 contains 10 wt % silver and calcium fluoride/barium fluoride eutectic while PS212 contains 15 percent of each. The coatings have almost identical friction and wear properties, but PS212 is currently favored because it exhibits slightly lower friction than PS200. These coatings have been successfully tested as

backup lubricants for compliant (foil) gas bearings, as cylinder liner coating material for the Stirling engine, and as valve guide material for process control valves. They can be plasma sprayed onto nickel and cobalt base super alloys and PS212 has been directly sprayed onto PSZ thermal barrier coatings. The duplex coating has the advantage of providing the dual function of providing thermal insulation and lubrication over a very broad temperature spectrum.

Recently, PM212, a powder metallurgy version of this material, has been developed at NASA Lewis Research Center. Free-standing parts have been prepared both by sintering and also by hot isostatic pressing (HIPing). The results of pin on disk studies of sintered PM212 are presented.

MATERIAL PREPARATION

Plasma-Sprayed PS212

The plasma-spray procedure for PS212 has been described elsewhere (Refs. 2 to 4). The sintering and HIP procedures for the powder metallurgy composites of the same chemical composition as PS212 are summarized below.

Sintered PM212

A schematic diagram of the procedure used in preparing sintered PM212 is shown in Fig. 1. A commercial blend of chromium carbide with a nickel-cobalt alloy binder is mixed with silver and calcium fluoride/barium fluoride eutectic in a Vee blender. The composition by weight percent is: 70 metal bonded chromium carbide-15 silver-15 eutectic. A green compact of the powders can be prepared by cold pressing in a die or by cold isostatic pressing (CIP). Our compacts were prepared by the CIP process. The powder is first poured into a rubber mold which is then evacuated with a vacuum pump. The mold is then sealed under vacuum, placed in a perforated aluminum support container, and immersed in a liquid

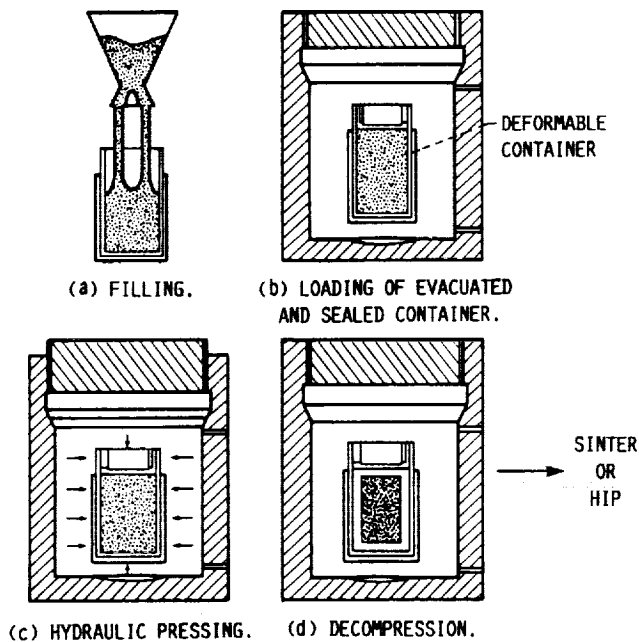


FIGURE 1. - STAGES IN COLD ISOSTATIC PRESSING.

pressure chamber. The powders are compacted hydraulically at high pressure. The cold pressed compact is then removed from the mold and sintered to increase the strength of the compact. Sintering is done at high temperature in a dry hydrogen atmosphere. Care must be exercised to maintain a low dew point in the hydrogen atmosphere to avoid the formation of chromium oxide during the sintering process. A back scatter SEM picture of the sintered composite is given in Fig. 2. Porosity and the various components of PS212 can all be discerned in this picture. Sintered PM212 contains about 20 percent pore space.

Hot Isostatically Pressed PM212

As indicated in Fig. 3, the blended powder can either be HIPed directly or it can be first compacted by the CIP process, then HIPed. We chose to pre-compact the blended powder by the CIP process. The green compact is then removed from the rubber mold, wrapped in graphoil, and placed in a thin steel can. The can is then vacuum sealed, and placed into a pressure vessel. The vessel is filled with high pressure argon gas and heated to the sintering temperature. After a prescribed time at temperature, the gas pressure and temperature are returned to ambient conditions and the can is removed from the chamber. The compacts made by this process are fully dense. The density is 6.60 g/cm^3 . The density difference of the sintered and HIPed materials are shown in Fig. 4. Photomicrographs of the diamond ground surface of sintered PM212 (Fig. 5) show the fluoride eutectic distributed throughout the carbide and metal matrix. Photographs taken with different types of

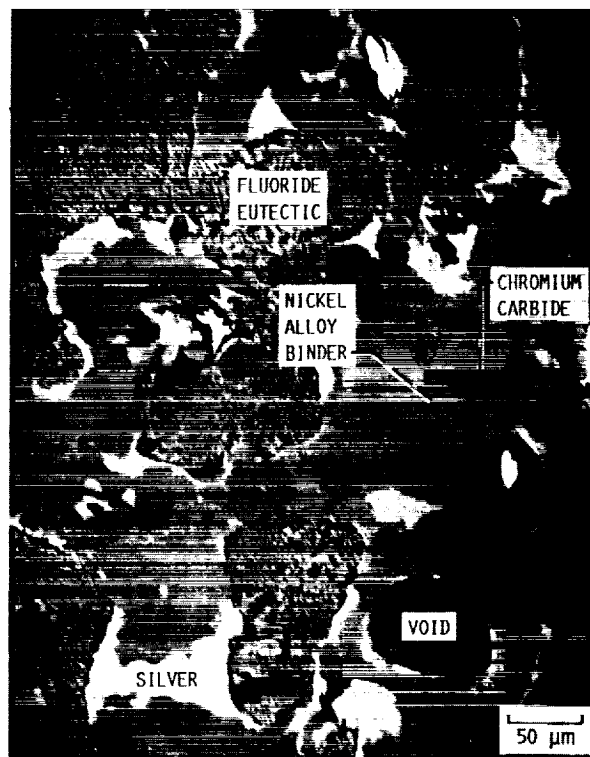
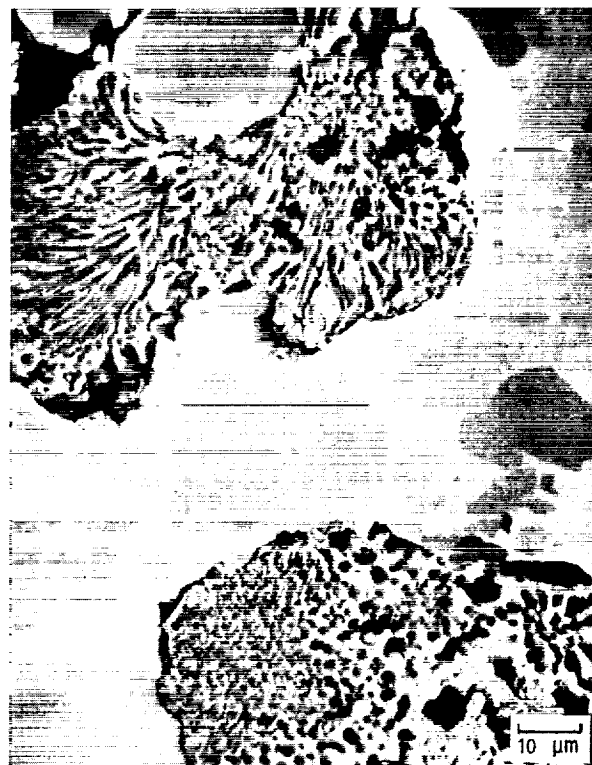


FIGURE 2. - DISTRIBUTION OF COMPONENTS IN SINTERED PM212.

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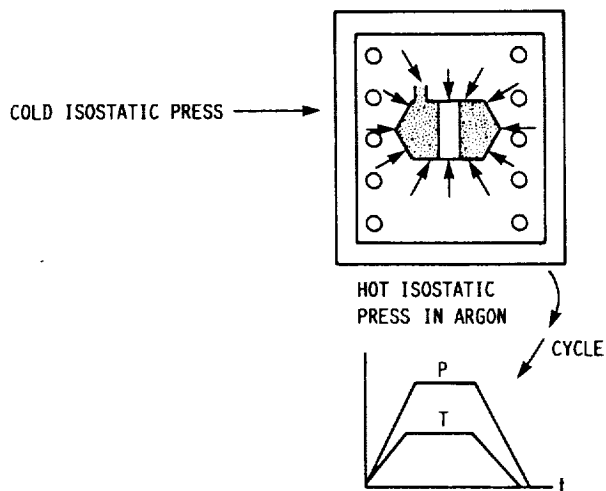
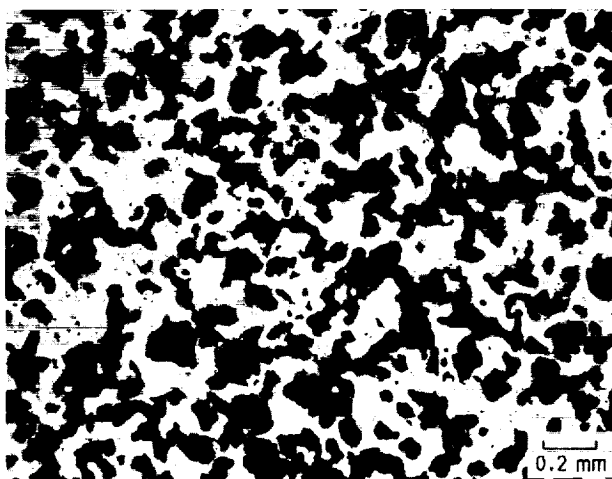
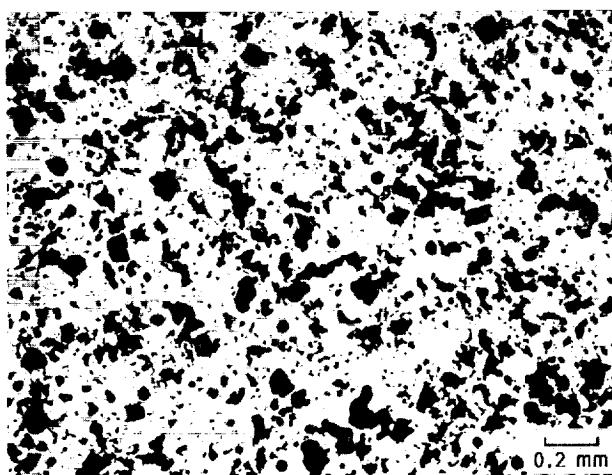


FIGURE 3. - STAGES IN HOT ISOSTATIC PRESSING.

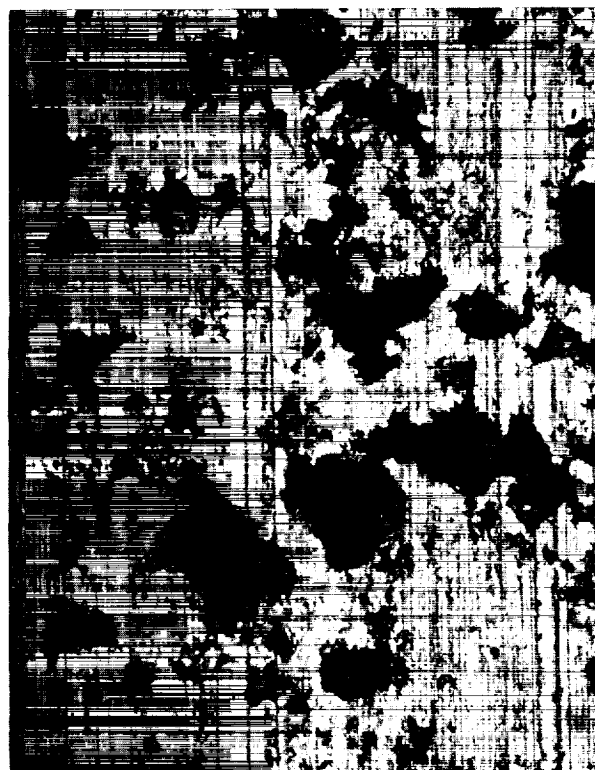


(a) PM212-CS.

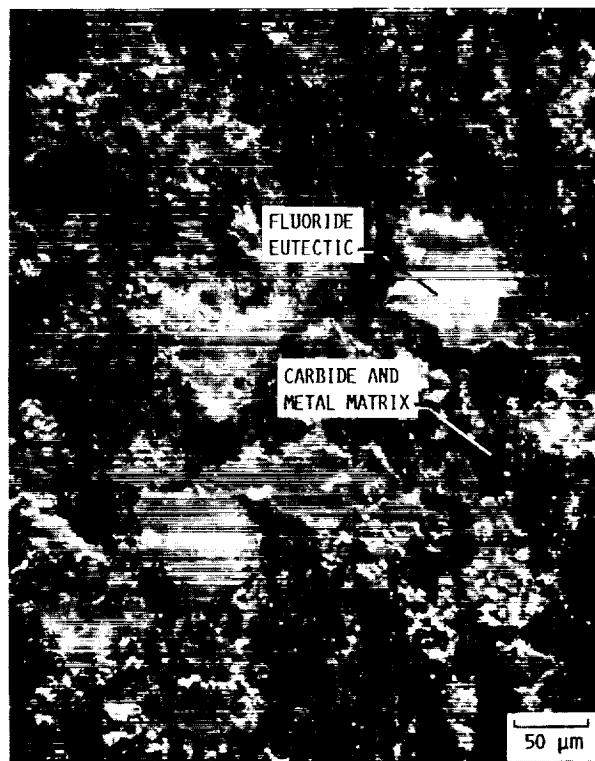


(b) PM212-CH.

FIGURE 4. - ILLUSTRATION OF DENSITY DIFFERENCE.



(a) VERTICAL ILLUMINATION.



(b) OBLIQUE ILLUMINATION.

FIGURE 5. - HIPPED PM212 MICROSTRUCTURE BY OPTICAL MICROSCOPY.

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illumination are shown to illustrate that the translucent fluorides cannot be differentiated from porosity when vertical illumination is employed, but they are imaged very well under oblique illumination.

The compressive strength of sintered and HIPed PM212 to 900 °C are shown in Fig. 6. The HIPed version is about three times stronger than the sintered version, but both materials retain strength to at least 700 °C that exceeds or equals the room temperature strength of many grades of bronze and carbon sliding contact bearing materials.

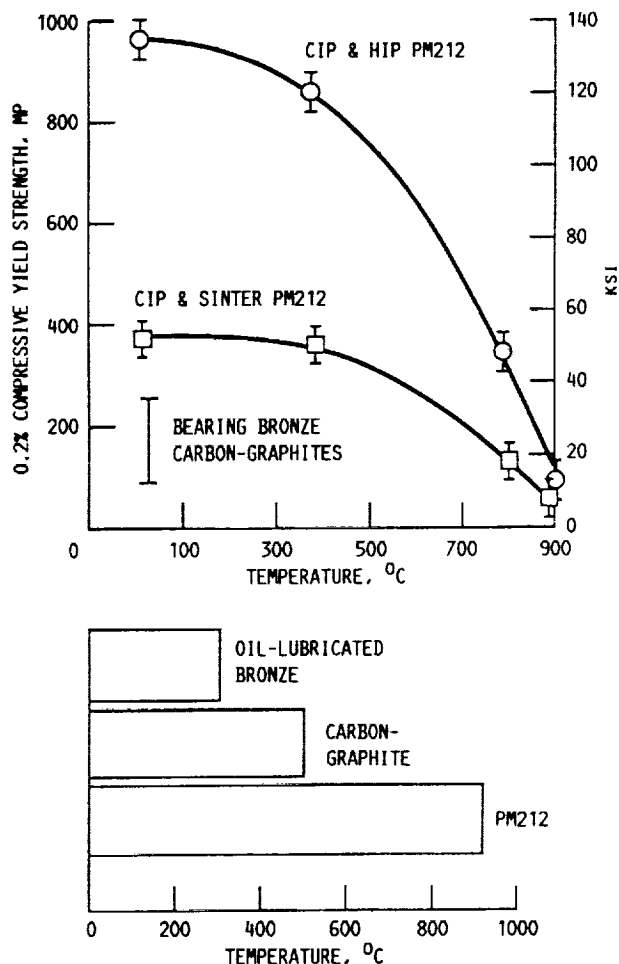


FIGURE 6. - STRENGTH AND MAXIMUM SERVICE COMPARISON OF PM212 WITH CONVENTIONAL BEARING MATERIALS.

Machining

Depending upon the precision to which the sintered parts or isostatically pressed parts can be processed during their preparation, either very little or quite extensive machining may be required. Parts that are cold mechanically pressed in a precision die before sintering may require no more than a mild deformation sizing step to achieve accurate

dimensions. Our parts, that were made from sintered or HIPed blanks, required extensive machining. The most successful process that we found for these materials consists of electrical discharge machining (EDM), followed by diamond grinding of surfaces that are to be the sliding contact bearing surfaces. Diamond grinding was the best finishing method found to insure that the softer phases in the composite are not selectively removed during the finishing process. Some machined PM212 parts are shown in Fig. 7.

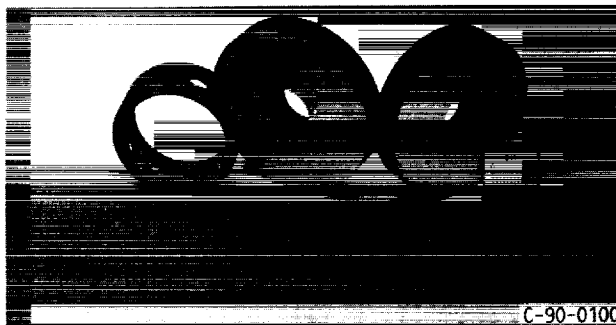


FIGURE 7. - PM212 PARTS FABRICATED BY EDM.

FRICITION AND WEAR RESULTS

Comparative tests of the friction and wear properties of the sintered composite and the plasma-sprayed coating were performed (Ref. 5). In the coating experiments, René 41 pins with a 4.76-mm radius tip were slid against Inconel 718 disks coated with PS212 that had been diamond ground to a thickness of 0.25 mm. In tests of the sintered material, PM212 pins were slid against uncoated René 41 disks.

The friction coefficients of the composite/metal couples are similar to those obtained with metal/coating couples. This is illustrated in Fig. 8 where the friction/temperature characteristics of the two combinations are compared. The experiments were conducted in air, with a 4.9-N load at 1000 rpm (2.7 m/s). The friction coefficient was very stable within a range of 0.3 to 0.35 from room temperature to 850 °C. Wear factors for the composite pins and René 41 disks are given in Table I.

The effect of load on friction followed Amonton's law from 4.9 to 29.4 N, i.e.: The friction force increased proportionately to the applied load. The wear factors also did not change significantly within that load range. The contact pressure for a 29.4-N load and a typical wear scar diameter of 1.3 mm is 22 MPa or about 3000 psi. Therefore, although the dynamic load capacity of PS212 was not determined, it was higher than 22 MPa at a sliding velocity of 2.7 m/s.

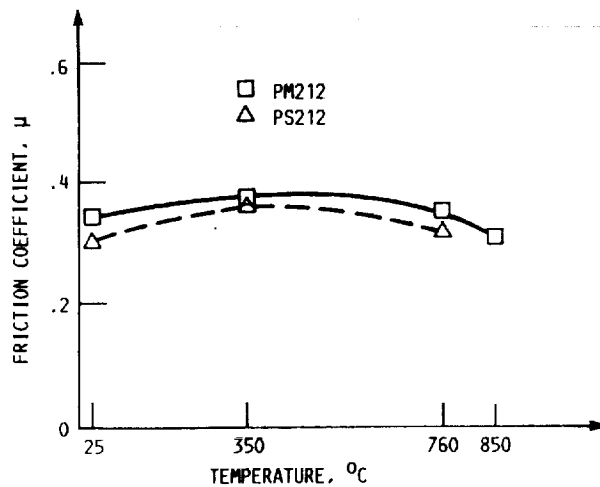


FIGURE 8. - FRICTION COEFFICIENT COMPARISON OF PM212 AND PS212 (PLASMA SPRAYED COATING) IN AIR, 35 PERCENT R.H. AT 25 °C, 0.5 kg LOAD, 2.7 m/s SLIDING VELOCITY.

TABLE I. - DATA SUMMARY

Temperature, °C	Load, kg	Friction coefficient, μ	KPM212, mm^3/Nm	KRené 41, mm^3/Nm	Number of tests
850	0.5	0.29 ± 0.03	$4.1 \pm 2.0 \times 10^{-6}$	$5.0 \pm 1.0 \times 10^{-6}$	2
760		$.35 \pm 0.06$	$3.6 \pm 0.9 \times 10^{-6}$	$1.0 \pm 6 \times 10^{-5}$	4
350		$.38 \pm 0.02$	$3.9 \pm 1.8 \times 10^{-5}$	$3.5 \pm 1.0 \times 10^{-6}$	3
25		$.35 \pm 0.05$	$3.2 \pm 1.5 \times 10^{-5}$	$7.0 \pm 2.0 \times 10^{-5}$	2

^aFriction and wear increase after ≈ 8 km of sliding at 350 °C. Friction increases to ≈ 0.5 and the pin material transfers to surface of disk.

The effect of sliding velocity on the friction coefficient of sintered PM212 is given in Fig. 9. At 760 and 900 °C, the friction coefficient decreases with increasing sliding velocity and is 0.2 at the highest velocity of 8.1 m/s. Friction behavior is less straightforward at lower temperatures, but is typically 0.3 to 0.35 except at the lowest sliding velocity at room temperature. At the other velocity extreme, the trend of decreasing friction with increasing sliding velocity suggests that friction coefficients considerably lower than 0.2 may be expected at sliding velocities typical of high speed shaft seals in turbomachinery.

The influence of sliding velocity on reducing friction is probably due to the increased localized frictional heating at high sliding velocities. This localized heating can be expected to soften the silver and fluoride surface films, thus reducing their shear strength without appreciably reducing the hardness and flow pressure of the material below the near-surface region.

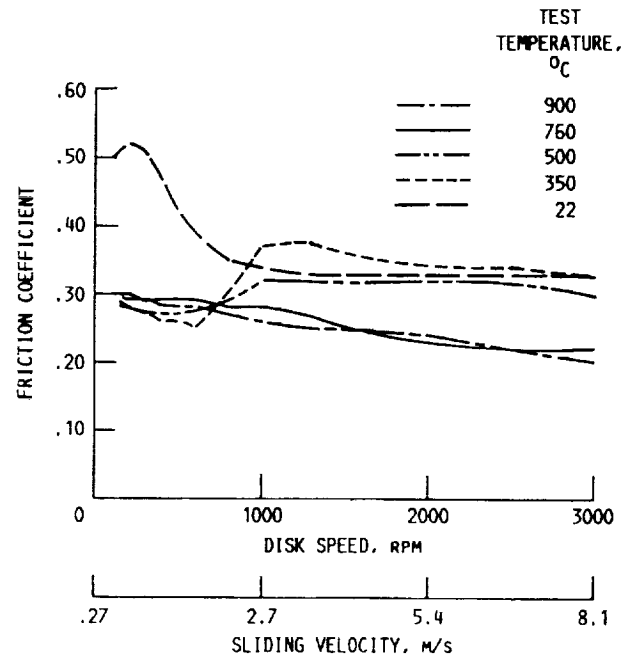


FIGURE 9. - FRICTION COEFFICIENT VERSUS SLIDING VELOCITY, 0.5 kg LOAD, IN AIR, 35 PERCENT R.H.

It was observed that the surface finish of diamond ground PS212 improved during sliding. Because of surface porosity of the coatings, even finish ground surfaces had a rms surface finish of about 0.8 μm initially but this was reduced typically to about 0.2 after sliding. The same phenomenon was observed with sintered PM212. Figure 10 shows that this was caused by closing of the surface pores and densification of the material under the sliding contact.

TECHNOLOGY TRANSFER

There has been considerable interest in the possible use of PS200 and PS212 in industrial applications. These coatings have been successfully tested for a number of applications such as:

- A backup lubricant for gas bearings
- A valve stem coating for gas flow control valves
- A cylinder liner coating for an automotive Stirling engine
- A low friction material for gas turbine, high-speed shaft seals
- A combustion chamber liner for rotary engines

A gas bearing journal and thrust ring coated with PS212 are shown in Fig. 11. PS212 journal coatings have lubricated foil gas bearings during start/stop tests at temperatures up to 700 °C (Ref. 4). The bearings.

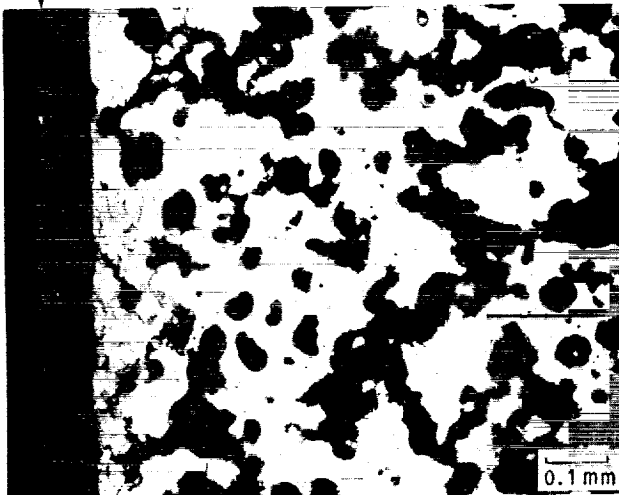
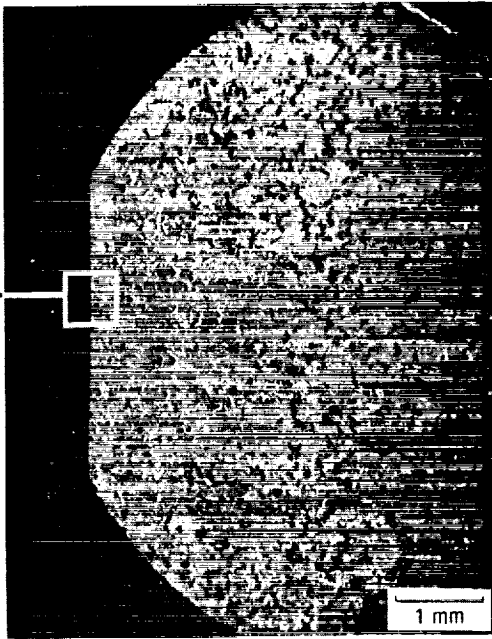


FIGURE 10. - SURFACE DENSITICATION OF PM212-CS ON A WEAR SCAR.

which are made of 0.013 cm thick Inconel X-750, were still in good condition after 20 000 start/stops over a programmed repetitive temperature cycle from room temperature to 700 °C.

We have previously reported promising results with PS200 coatings on Stirling engine cylinder walls (Ref. 6). An engine of the design shown in Fig. 12 was tested for over 20 hr with Stellite 6B piston rings sliding against the coating in a hydrogen atmosphere at a top ring reversal cylinder wall temperature of 700 °C.

As previously stated, the friction coefficients of these composite materials tend to decrease with increasing sliding velocity.

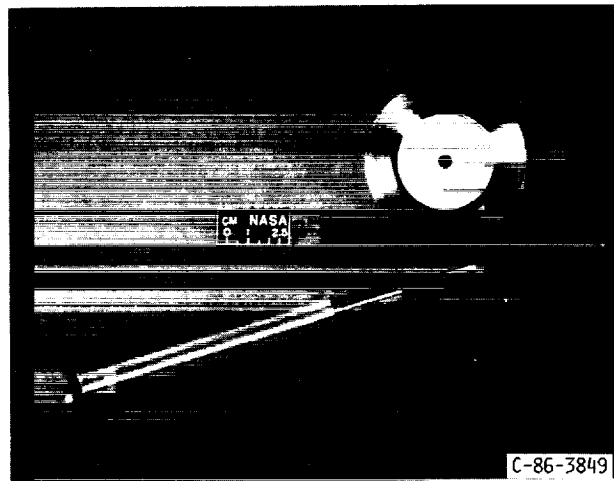


FIGURE 11. - HIGH SPEED GAS BEARING JOURNAL AND THRUST PLATE COATED WITH PS212.

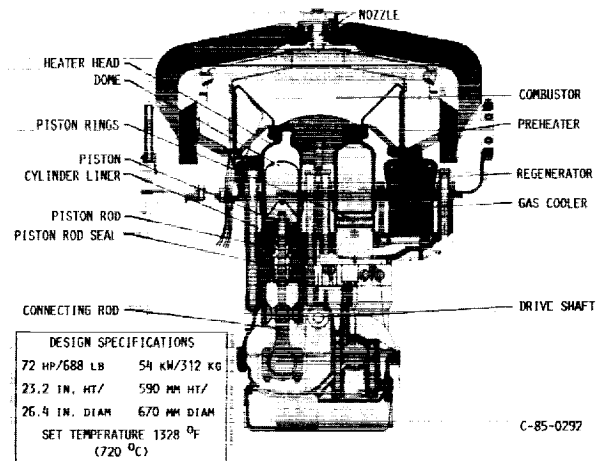


FIGURE 12. - AUTOMOBILE STIRLING ENGINE.

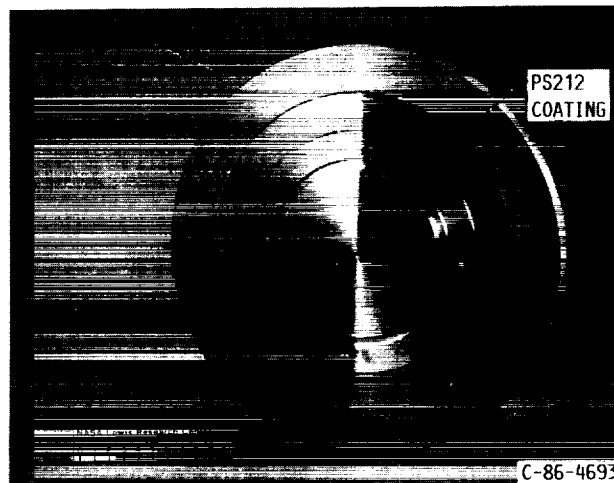


FIGURE 13. - HIGH SPEED SHAFT SEAL WITH PS212 COATING ON SEAL SURFACE.

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Therefore, low friction and wear can be expected during high speed, high temperature operation of PS200 or PS212 coated components such as the turbine shaft seal shown in Fig. 13.

Recently, PS212 has been tested as the top coat of a duplex coating for rotary engines. Figure 14 is a schematic drawing of a rotary engine rotor and combustion chamber. The engine housing is an aluminum alloy and therefore is very temperature limited. A thermal barrier coating (TBC) on the side walls and the trochoid surface of the combustion chamber should allow higher power density without overheating the engine housing. Partially stabilized zirconia is a good TBC but has poor tribological properties in contact with the rotor apex seals and side seals. Therefore, a two-layer coating was prepared. It consisted of 0.05 cm thick PSZ coating with a top coat of PS212 diamond ground to a thickness of 0.015 cm. The PS212 was sprayed directly onto the PSZ to form a duplex coating with the necessary combination of insulating ability and good tribological properties. Satisfactory adhesion was achieved without the necessity of a graded composition between the PSZ and PS212.

To provide an internal comparison of the coated wall with an uncoated one, only one side wall of the combustion chamber was coated as shown in Fig. 14. Thermocouples were

inserted at various depths in the walls and temperature gradients in the two side walls were compared during engine operation.

The major results were: (1) The measured temperatures of the insulated side wall were about 28 °C (50 °F) lower than those in the uninsulated wall during full throttle fired engine operation. (2) There was no measurable wear on either the coating or the side seals after 20 hr of full power operation. This evaluation demonstrated the feasibility of the dual coating concept. In order to determine the effect on power and efficiency, it will be necessary to test engines with the duplex coating on all of the internal surfaces of the combustion chamber.

CONCLUSIONS

1. Coatings and powder metallurgy composites of metal-bonded chromium carbide with dispersed silver and $\text{CaF}_2/\text{BaF}_2$ eutectic are self-lubricating materials from low temperatures to 900 °C. The best composition so far evaluated is by weight percent: 70 bonded carbide-15 silver-15 fluoride eutectic. The coatings are designated as PS212 and the powder metallurgy compacts as PM212.

2. The coatings and the free-standing powder metallurgy compacts are complementary in their applicability. The powder metallurgy

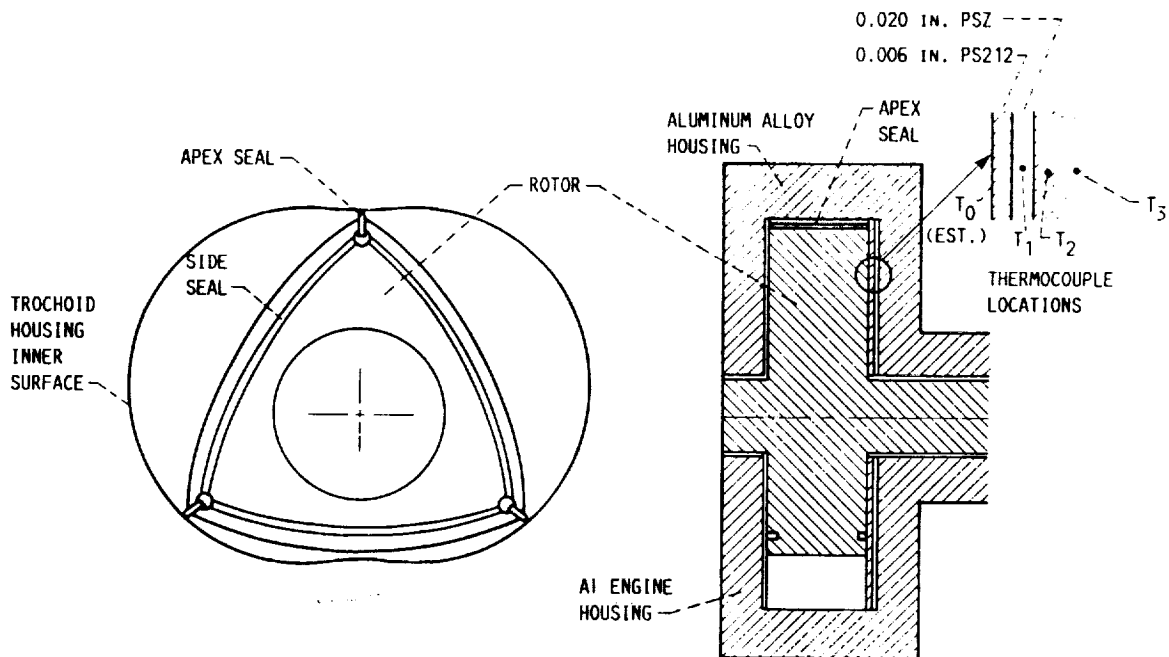


FIGURE 14. - SCHEMATIC OF PS212/PSZ DUPLEX COATING FOR COMBINED TRIBOLOGICAL AND THERMAL BARRIER BENEFITS IN ROTARY ENGINES. (COATING IS ON ONLY ONE SIDE WALL OF EXPERIMENTAL ENGINE FOR COMPARISON OF THERMAL GRADIENTS WITH UNCOATED SIDE WALL.)

processes can easily produce parts with surfaces that are very difficult to spray as, for example, small bore cylindrical bearings.

3. The compressive strength of sintered PM212 from room temperature to 760 °C compares favorably to the room temperature strength of many common grades of bronze and carbon sliding contact bearing materials. HIPed PM212 is about three times stronger than the sintered version, probably because it is fully dense while the sintered material contains 20 percent porosity.

4. The friction coefficients of PS212 and PM212 decrease with increasing sliding velocity making them promising candidates as high-speed, high-temperature sliding contact seal materials.

5. PS212 can be directly plasma sprayed to form an adherent top coat on zirconia thermal barrier coatings to form a duplex coating with a desirable combination of thermal insulation and self-lubricating properties.

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